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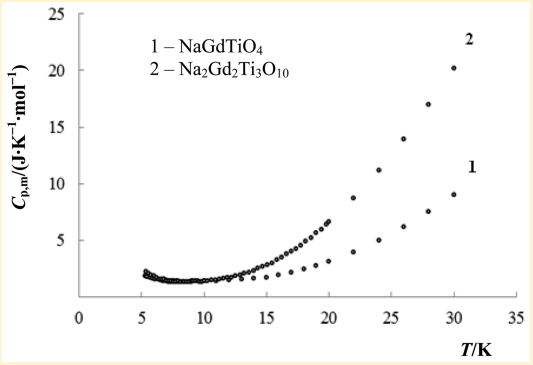
Heat Capacity and Standard Thermodynamic Functions of $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ over the Range from (6 to 630) K

Alexey V. Markin,*[,†] Anna M. Sankovich,[†,‡] Natalia N. Smirnova,[†] and Irina A. Zvereva[‡]

[†]Lobachevsky State University of Nizhni Novgorod, 23/5 Gagarin Avenue, 603950, Nizhni Novgorod, Russia

[‡]St. Petersburg State University, 26 Universitetsky Avenue, Petrodvorets, 198504, St. Petersburg, Russia

ABSTRACT: The heat capacities of layered perovskite-like oxides $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ were measured by precision adiabatic vacuum calorimetry over the temperature range from T = (6 to 344) K and by differential scanning calorimetry over the temperature range from T = (320 to 630) K. The standard thermodynamic functions: molar heat capacity $C^{\circ}_{p,m}$, enthalpy $H^{\circ}(T) - H^{\circ}(5)$, entropy $S^{\circ}(T) - S^{\circ}(5)$, and Gibbs energy of the compounds were evaluated from the experimental heat capacity temperature dependences over the range from T = (5 to 630) K.



INTRODUCTION

Layered perovskite-like oxides are the objects of close attention because they are one of the promising classes of ceramic materials. Compounds with this crystal structure exhibit remarkable physicochemical properties, such as very large magnetoresistance,[1] multiferroism,[2] high-temperature superconductivity,[3] catalytic and photocatalytic activity,[4−6] and ion exchange properties.[7]

The knowledge of thermophysical properties for these materials would facilitate their practical application in various branches of chemical engineering and electronics. Moreover, it would be valuable from the theoretical point of view. However, high-quality thermodynamic data available in the literature[8−11] for this class of compounds are scarce.

The purpose of the present paper is to report the results of calorimetric investigation of layered perovskite-like titanates $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ over the temperature range from T = (6 to 630) K. These oxides belong to the Ruddlesden−Popper phases[12] $(Na,Gd)_{n+1}Ti_nO_{3n+1}$, where n is a number of perovskite layers. Interest in the above oxides is motivated by their use as catalysts for photoinduced reactions and precursors for synthesis of other layered compounds via ion exchange and topochemical routes.[13]

EXPERIMENTAL SECTION

Synthesis and Characterization of Layered Perovskite-like Oxides. The layered perovskite-like oxides $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ were obtained according to the conventional ceramic technology[14] through the reactions:

$$Na_2CO_3 + 2TiO_2 + Gd_2O_3 \rightarrow 2NaGdTiO_4 + CO_2 \quad (1)$$

$$Na_2CO_3 + 3TiO_2 + Gd_2O_3 \rightarrow Na_2Gd_2Ti_3O_{10} + CO_2 \quad (2)$$

The following reactants (Johnson Matthey) were used as the initial compounds: gadolinium oxide Gd_2O_3 (the content of the main component was 99.95 %) preliminarily calcined at T = 1173 K for 5 h in order to remove moisture, finely dispersed titanium oxide TiO_2 (99.9 %) in the anatase modification, and sodium carbonate Na_2CO_3 (99.5 %). The reactants were carefully mixed in an agate mortar (on the basis of 40 min of grinding per gram of the initial mixture). The prepared batch mixture was pressed into pellets of 0.5 g in weight and 0.7 cm in diameter. The samples were sintered in a Nabertherm HTCT 01/16 high-temperature furnace in corundum crucibles at atmospheric pressure in air. The temperature conditions were controlled by a platinum−rhodium thermocouple. The isothermal conditions of heat treatment were ensured to be standard uncertainty for temperature $u(T)$ = 1 K with the use of a TP-403 programmable temperature controller. $NaGdTiO_4$ was synthesized at temperature T = 1073 K for 4 h, $Na_2Gd_2Ti_3O_{10}$, at T = 1273 K for 10 h.

Characterization of the samples was provided by X-ray powder diffraction analysis and optical emission spectrometry analysis. Qualitative X-ray powder diffraction analysis of the samples was performed on a Rigaku MiniFlex II diffractometer (Cu $K\alpha$ radiation). The XRD patterns (Figure 1) were recorded under the following conditions: 2θ = 5° to 60° at a step of 0.02° and a rate of 2° per min. The phase composition of the samples was determined using the ICDD PDF-2 Database. Optical emission spectrometer ICPE-9000 (Shimadzu, Japan) was used to determine qualitative composition of the samples. No significant

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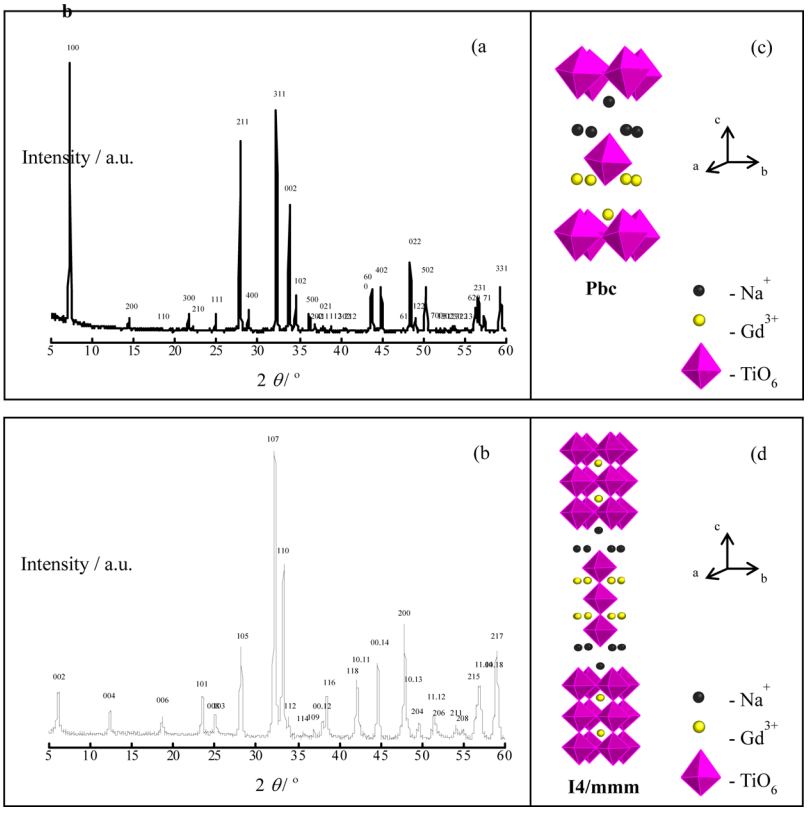

Figure 1. X-ray diffraction patterns of $NaGdTiO_4$ (a) and $Na_2Gd_2Ti_3O10$ (b). 2θ is a scattering angle.

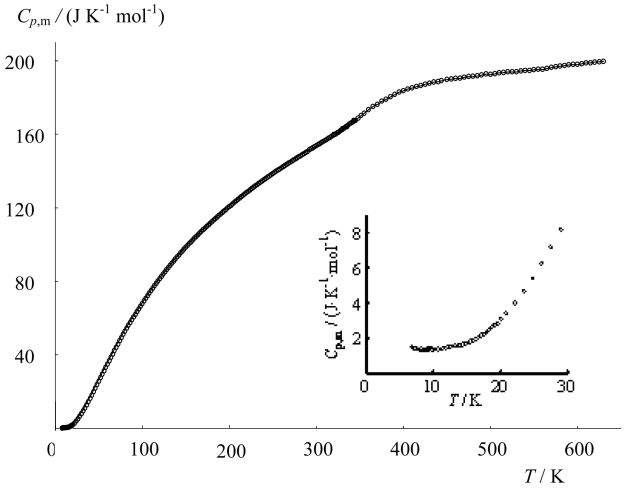

Figure 2. Experimental molar heat capacity $C_{p,m}$ of $NaGdTiO_4$ as a function of temperature.

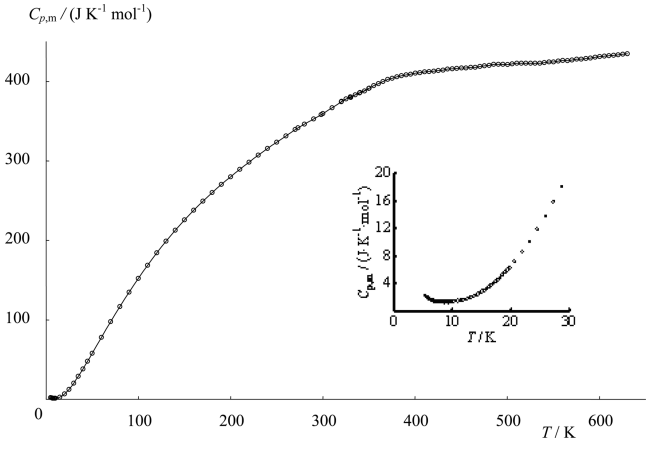

Figure 3. Experimental molar heat capacity $C_{p,m}$ of $Na_2Gd_2Ti_3O_{10}$ as a function of temperature.

impurities were detected, the sensitivity limit is 10^{-9} to 10^{-8}. It is observed that all diffraction peaks match well with the standard data of $NaGdTiO_4$ (ICDD PDF-2 No. 01-086-0830) or those of $Na_2Gd_2Ti_3O_{10}$ (ICDD PDF-2 No. 01-086-1372) in our experimental range. No impurity diffraction peaks were found.

The crystal structures of $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ are displayed in Figure 2 panels c and d, respectively. $NaGdTiO_4$ belongs to the orthorhombic tetragonal system with the space group *Pbcm* (57) and the symmetry of $Na_2Gd_2Ti_3O_{10}$ is tetragonal *I4/mmm* (139). It can be seen that the crystal structures consist of single ($NaGdTiO_4$) or triple ($Na_2Gd_2Ti_3O_{10}$)

Table 1. Sample Information

chemical name	source	state	mole fraction purity	analysis method
$NaGdTiO_4$	present work	powder	0.98	X-ray fluorescence spectrometry, X-ray powder diffraction, optical emission spectrometry, thermogravimetric analysis
$Na_2Gd_2Ti_3O_{10}$	present work	powder	0.98	X-ray fluorescence spectrometry, X-ray powder diffraction, optical emission spectrometry, thermogravimetric analysis

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Table 2. Experimental Molar Heat Capacity $C_{p,m}$ of Crystalline $NaGdTiO_4$ (M = 292.10 g·mol^{-1})[a]

T / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}
series 1					
6.81	1.52	13.62	1.59	34.79	12.79
6.98	1.45	14.00	1.61	36.29	14.04
7.18	1.42	14.38	1.64	37.81	15.37
7.38	1.41	14.76	1.70	39.34	16.74
7.58	1.37	15.15	1.74	40.89	18.06
7.78	1.37	15.52	1.81	42.45	19.50
7.98	1.35	15.92	1.90	44.02	20.95
8.17	1.38	16.31	1.95	45.60	22.45
8.37	1.33	16.71	2.05	47.19	23.92
8.56	1.33	17.11	2.17	48.79	25.45
8.75	1.34	17.51	2.24	50.40	27.01
8.94	1.36	17.92	2.36	52.02	28.57
9.13	1.38	18.33	2.50	53.64	30.04
9.32	1.38	18.74	2.67	55.27	31.51
9.51	1.39	19.17	2.76	56.91	33.04
9.71	1.39	19.59	2.86	58.55	34.55
9.89	1.35	20.01	3.095	60.20	36.04
10.08	1.38	20.85	3.434	61.85	37.52
10.35	1.39	22.13	4.020	63.50	39.02
10.70	1.39	23.43	4.694	65.16	40.72
11.05	1.39	24.77	5.427	66.82	41.92
11.40	1.42	26.13	6.260	68.49	43.51
11.76	1.44	27.52	7.200	70.16	45.10
12.12	1.50	28.93	8.195	72.24	46.90
12.49	1.53	30.36	9.286	74.73	49.06
12.86	1.55	31.82	10.43	77.23	51.29
13.24	1.57	33.30	11.59	79.74	53.31
series 2					
80.89	53.93	157.85	103.0	234.70	133.9
83.89	56.40	160.41	104.2	237.26	134.7
86.41	58.39	162.98	105.4	239.82	135.7
88.93	60.35	165.54	106.6	242.39	136.5
91.45	62.32	168.11	107.7	244.95	137.4
93.98	64.24	170.67	108.8	247.51	138.2
96.51	66.14	173.24	110.0	250.08	139.1
99.05	67.93	175.80	111.3	252.64	139.8
101.59	69.81	178.36	112.2	255.21	140.7
104.12	71.60	180.93	113.2	257.77	141.4
106.67	73.34	183.49	114.4	260.33	142.2
109.21	75.05	186.05	115.5	262.89	143.0
111.76	76.80	188.60	116.6	265.45	143.7
114.31	78.47	191.16	117.5	268.01	144.5
116.86	80.11	193.72	118.6	270.57	145.3
119.41	81.69	196.28	119.6	273.12	146.0
121.98	83.34	198.84	120.6	275.68	146.8
124.53	84.90	201.40	121.6	278.23	147.5
127.09	86.43	203.95	122.8	280.77	148.2
129.65	87.87	206.51	123.6	283.32	149.0
132.21	89.41	209.07	124.6	285.84	149.8
134.77	90.90	211.63	125.6	288.38	150.5
137.33	92.37	214.19	126.6	290.92	151.2
139.90	93.76	216.75	127.5	294.66	152.0
142.46	95.16	219.31	128.4	297.49	152.5
145.03	96.47	221.87	129.5	300.00	153.9
147.59	97.84	224.44	130.4	302.86	154.4
150.15	99.20	227.00	131.3	306.18	155.4
152.72	100.5	229.56	132.6	309.48	156.3
155.28	101.7	232.13	133.1	312.78	157.3
316.05	158.3	329.14	162.4	342.12	167.3
319.33	159.2	332.40	163.5	345.34	168.7
322.61	160.3	335.65	164.7		
325.88	161.4	338.89	166.0		
DSC					
320.1	160	425.1	187	530.1	194
325.1	161	430.1	188	535.1	195
330.1	163	435.1	188	540.1	195
335.1	164	440.1	189	545.1	195
343.1	168	443.8	189	550.1	195
348.1	169	450.1	190	555.1	195
351.3	170	455.1	190	560.1	195
355.1	172	460.1	190	565.1	196
360.1	173	465.1	191	570.1	196
365.1	175	470.1	191	575.1	197
370.1	176	475.1	192	580.1	197
375.1	178	480.1	192	585.1	197
380.1	179	485.1	192	590.1	198
385.1	180	490.1	192	595.1	198
390.1	182	495.1	193	600.1	198
395.1	183	500.1	193	605.1	198
400.1	184	505.1	193	610.1	199
405.1	185	510.1	193	615.1	199
410.1	185	515.1	194	620.1	199
415.1	186	520.1	194	625.1	199
420.1	187	525.1	194	630.1	199

[a]The standard uncertainty for temperature $u(T)$ = 0.01 K in the temperature range from T = (6 to 350) K, and $u(T)$ = 0.5 K in the interval between T = (320 and 630) K. The relative standard uncertainty for heat capacity $u_r(C_{p,m})$ = 0.02 in the temperature range from T = (6 to 15) K, $u_r(C_{p,m})$ = 0.005 between T = (15 to 40) K, $u_r(C_{p,m})$ = 0.002 in the temperature range from T = (40 to 350) K, and $u_r(C_{p,m})$ = 0.02 over the range from T = (320 to 630) K.

perovskite-like slab layers stacked along the [001] direction which are separated by the rock-salt type double layers. The last are presented by (NaO) and (GdO) layers in the case of $NaGdTiO_4$ and (NaO) layer for $Na_2Gd_2Ti_3O_{10}$.

The chemical analysis of the investigated titanates was carried out on the energy dispersive X-ray fluorescence spectrometer EDX-900HS (Shimadzu, Japan). From the experimental data it was found that the ratio of elements Ti/Gd is equal to 0.98:1.02, and 2.99:2.01 for $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$, respectively. Additionally, the obtained results allow excluding nonstoichiometric oxygen in the studied samples.

According to the thermogravimetric (TG) analysis carried out by us, it was established that the samples were thermally stable in the studied temperature range (until T = 673 K).

The information for the studied titanates is listed in Table 1.

The molar masses of $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ were calculated from the International Union of Pure and Applied Chemistry (IUPAC) table of atomic weights.[15]

Adiabatic Calorimetry. A BCT precision automatic adiabatic calorimeter (Termis, Moscow) was used to measure isobaric heat capacities ($C_{p,m}$) of $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ over the temperature range of (6 to 350) K. The design and

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Table 3. Experimental Molar Heat Capacity $C_{p,m}$ of Crystalline $Na_2Gd_2Ti_3O_{10}$ (M = 664.07 g·mol^{-1})[a]

T / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}	T / K	$C_{p,m}$ / J·K^{-1}·mol^{-1}
series 1					
5.36	2.20	10.91	1.50	24.53	11.90
5.56	2.09	11.23	1.52	25.89	13.76
5.78	1.96	11.53	1.62	27.28	15.85
5.99	1.85	11.86	1.67	28.70	18.07
6.20	1.69	12.20	1.73	30.14	20.52
6.41	1.57	12.54	1.85	31.60	22.94
6.60	1.52	12.89	1.95	33.07	25.59
6.79	1.53	13.24	2.05	34.57	28.21
6.99	1.44	13.60	2.17	36.08	30.88
7.18	1.41	13.96	2.28	37.61	33.70
7.36	1.38	14.32	2.49	39.16	36.60
7.55	1.36	14.68	2.67	40.71	39.57
7.73	1.33	15.06	2.84	42.28	42.56
7.91	1.38	15.43	2.98	43.85	45.69
8.09	1.36	15.81	3.24	45.44	48.89
8.27	1.34	16.19	3.49	47.04	52.01
8.45	1.35	16.58	3.76	48.65	55.29
8.63	1.31	16.97	4.04	50.27	58.63
8.81	1.34	17.35	4.26	51.89	61.81
8.98	1.37	17.75	4.56	53.52	65.10
9.16	1.37	18.15	4.88	55.16	68.18
9.33	1.32	18.56	5.31	56.80	71.45
9.50	1.37	18.97	5.62	58.45	74.83
9.67	1.40	19.39	5.98	60.10	78.20
9.84	1.47	19.81	6.31	61.76	81.39
10.02	1.48	20.63	7.250	63.42	84.61
10.27	1.42	21.89	8.595	65.09	87.97
10.59	1.48	23.20	10.12	66.75	91.38
68.43	94.41	72.19	101.9	77.19	111.5
70.10	97.88	74.69	106.7	79.71	116.1
series 2					
81.46	119.0	150.95	227.2	221.16	299.5
84.37	124.7	153.54	230.3	223.77	301.8
86.89	129.3	156.13	233.6	226.39	304.0
89.41	133.8	158.72	236.7	229.01	306.9
91.94	138.2	161.31	239.7	231.63	308.9
94.48	142.6	163.92	242.6	234.25	310.7
97.02	147.1	166.51	245.5	236.88	312.8
99.56	151.4	169.10	248.4	239.50	315.0
102.11	155.8	171.70	251.3	242.13	317.4
104.65	160.0	174.29	254.0	244.76	319.6
107.21	164.1	176.88	256.9	247.42	321.8
109.76	168.2	179.48	259.6	250.05	323.8
series 2					
112.32	172.2	182.08	262.3	252.68	326.0
114.88	176.3	184.67	265.0	255.31	328.0
117.44	180.2	187.27	267.6	257.95	330.0
120.01	184.2	189.87	270.2	260.58	332.2
122.59	188.1	192.47	272.6	263.21	334.1
125.16	192.0	195.06	275.2	265.85	336.0
127.74	195.7	197.66	277.9	268.48	338.1
130.31	199.4	200.26	280.4	271.12	339.9
132.89	203.1	202.87	282.7	273.75	341.7
135.46	206.7	205.49	285.4	276.38	343.7
138.04	210.3	208.10	287.7	279.02	345.8
140.62	213.8	210.71	290.1	281.65	347.3
143.20	217.3	213.32	292.4	284.28	349.1
145.78	220.6	215.93	295.0	286.90	351.1
148.37	223.9	218.54	297.2	289.55	353.1
292.17	354.6	309.92	366.4	330.43	379.2
294.79	356.2	313.33	369.1	333.86	380.8
297.41	357.9	316.75	372.0	337.27	383.0
300.01	359.8	320.16	374.9	340.68	385.8
303.06	361.7	323.58	377.7	344.09	386.9
306.49	363.8	326.99	378.5		
DSC					
320.3	375	425.3	414	530.3	423
325.3	378	430.3	414	535.3	423
330.3	380	435.3	416	540.3	424
335.3	383	440.3	416	545.3	425
340.3	386	445.3	416	550.3	425
345.3	388	450.3	417	555.3	426
350.3	391	455.3	417	560.3	426
355.3	395	460.3	418	565.3	426
360.3	397	465.3	418	570.3	427
365.3	400	470.3	419	575.3	428
370.3	403	475.3	420	580.3	428
375.3	404	480.3	420	585.3	429
380.3	406	485.3	422	590.3	429
385.3	407	490.3	422	595.3	430
390.3	408	495.3	422	600.3	431
395.3	409	500.3	421	605.3	432
400.3	411	505.3	422	610.3	433
405.3	411	510.3	423	615.3	433
410.3	412	515.3	423	620.3	434
415.3	412	520.3	423	625.3	434
420.3	413	525.3	423	630.3	435

[a]The standard uncertainty for temperature $u(T)$ = 0.01 K in the temperature range from T = (5 to 344) K, and $u(T)$ = 0.5 K in the interval between T = (320 and 630) K. The relative standard uncertainty for heat capacity $u_r(C_{p,m})$ = 0.02 in the temperature range from T = (6 to 15) K, $u_r(C_{p,m})$ = 0.005 between T = (15 to 40) K, $u_r(C_{p,m})$ = 0.002 in the temperature range from T = (40 to 350) K, and $u_r(C_{p,m})$ = 0.02 over the range from T = (320 to 630) K.

operation of the calorimeter were described in detail earlier.[16,17] The relative uncertainties in heat capacity measurements were $u_r(C_{p,m})$ = 0.02 at T < 15 K, $u_r(C_{p,m})$ = 0.005 over the temperature range of (15 to 40) K, and $u_r(C_{p,m})$ = 0.002 between T = (40 to 350) K. The accuracy of the calorimeter was verified using standard reference samples (benzoic acid and α-Al_2O_3).

A titanium calorimetric cell with a volume of 1.5 cm^3 was loaded with a sample and then degassed in vacuum with a residual pressure of ~5 Pa. Dry helium gas (at p = 4 kPa and room temperature) was introduced into the cell to facilitate heat transfer during the measurements. The sample masses used for calorimetric measurements were 1.3814 g of $NaGdTiO_4$ and 1.6506 g of $Na_2Gd_2Ti_3O_{10}$.

An iron−rhodium resistance thermometer placed on the inner surface of the adiabatic shield was used for the temperature measurements in the calorimetric experiments. The temperature difference between the cell and the shield was determined by a differential copper−iron−chromel thermocouple. The sensitivity of the thermometric circuit was 10^{-3} K.

After being assembled, the measuring system was cooled in a liquid nitrogen bath. If the measurements were performed below 80 K, a liquid helium bath was used. The samples were cooled to

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Table 4. Smoothed Molar Heat Capacity and Thermodynamic Functions of Crystalline $NaGdTiO_4$ (M = 292.10 g·mol^{-1}) at Pressure p = 0.1 MPa[a]

T	$C^\circ_{p,m}$	$[H^\circ(T) - H^\circ(5)]$	$[S^\circ(T) - S^\circ(5)]$	$-\Phi^\circ_m$[b]
K	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}
5	1.73	0	0	0
10	1.37	0.00720	1.00	0.00288
15	1.70	0.0147	1.62	0.00957
20	3.089	0.02660	2.284	0.01905
25	5.590	0.04830	3.2307	0.03246
30	8.998	0.08350	4.5153	0.05192
40	17.28	0.2157	8.2314	0.1136
50	26.62	0.4328	13.06	0.2199
60	35.85	0.7475	18.74	0.3772
70	44.94	1.150	24.94	0.5963
80	53.63	1.645	31.52	0.8771
90	61.35	2.219	38.29	1.227
100	68.62	2.870	45.13	1.643
110	75.62	3.591	52.01	2.130
120	82.09	4.381	58.86	2.683
130	88.14	5.231	65.68	3.307
140	93.80	6.142	72.42	3.996
150	99.09	7.106	79.07	4.755
160	104.0	8.122	85.62	5.578
170	108.6	9.184	92.07	6.468
180	112.9	10.29	98.40	7.419
190	117.1	11.44	104.6	8.435
200	121.0	12.63	110.7	9.511
210	125.0	13.86	116.7	10.65
220	128.7	15.13	122.6	11.84
230	132.3	16.44	128.4	13.10
240	135.7	17.78	134.1	14.41
250	139.0	19.15	139.7	15.78
260	142.1	20.56	145.3	17.21
270	145.1	21.99	150.7	18.69
280	148.1	23.46	156.0	20.22
290	150.9	24.95	161.3	21.81
298.15	153.2	26.19	165.5	23.14
300	153.7	26.48	166.4	23.45
310	156.5	28.03	171.5	25.14
320	159.5	29.61	176.5	26.88
330	162.7	31.22	181.5	28.67
340	166.2	32.86	186.4	30.50
350	170	34.5	191	32.4
360	173	36.3	196	34.3
370	176	38.0	201	36.3
380	179	39.8	206	38.3
390	182	41.6	210	40.4
400	184	43.4	215	42.6
410	185	45.3	219	44.7
420	186	47.1	224	46.9
430	188	49.0	228	49.2
440	189	50.9	233	51.5
450	190	52.8	237	53.9
460	190	54.7	241	56.2
470	191	56.6	245	58.7
480	192	58.5	249	61.2
490	192	60.4	253	63.7
500	193	62.3	257	66.2
510	193	64.3	261	68.8
520	194	66.2	265	71.4
530	194	68.1	268	74.1
540	195	70.1	272	76.8
550	195	72.0	276	79.5
560	195	74.0	279	82.3
570	196	75.9	283	85.1
580	197	77.9	286	88.0
590	198	79.9	289	90.8
600	198	81.9	293	93.8
610	199	83.9	296	96.7
620	199	85.8	299	99.7
630	200	87.8	302	103

[a]Standard for temperature $u(T)$ = 0.01 K in the temperature range from T = (5 to 344) K, and $u(T)$ = 0.5 K in the interval between T = (320 and 630) K. The standard uncertainty for pressure $u(p)$ = 10 kPa. Combined expanded uncertainties for the heat capacity $U_c(C_{p,m}{}^\circ)$ are 0.02, 0.005, 0.002, and 0.02; the combined expanded uncertainties $U_c[H^\circ(T) - H^\circ(5)]$ are 0.022, 0.007, 0.005, and 0.022; $U_c[S^\circ(T) - S^\circ(5)]$ are 0.023, 0.008, 0.006, and 0.023; $U_c[\Phi^\circ_m]$ are 0.03, 0.01, 0.009, and 0.03 in the ranges $6 \le T/K \le 15$, $15 \le T/K \le 40$, $40 \le T/K \le 344$, and $320 \le T/K \le 630$, respectively, for 0.95 level of confidence ($k \approx 2$). [b]$\Phi^\circ_m = [H^\circ(T) - H^\circ(5)] - T[S^\circ(T) - S^\circ(5)]$.

the temperature of the measurement onset at a rate of 10^{-2} K·s^{-1}. Then the samples were heated with a temperature step of (0.5 to 2) K at a rate of 10^{-2} K·s^{-1}. Sample temperature was recorded after an equilibration period (temperature drift < 10^{-2} K·s^{-1}, approximately 10 min per experimental point).

The ratio of the sample heat capacity to the total (sample + cell) one was between 0.6 to 0.8.

DSC and TG Analysis. Heat capacities of $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ over the range of (320 to 630) K were measured in a DSC 204 F1 Phoenix differential scanning calorimeter (Netzsch Gerätebau, Germany) with use of a μ-sensor. The calorimeter was calibrated and tested against melting of n-heptane, adamantane, indium, tin, bismuth, and zinc. The heat capacity was determined by the "ratio method", with sapphire used as a standard reference sample. The curves of heat capacities for both titanates were recorded three times at the repeated cooling and heating of each sample. The $C_{p,m}$ values were reproduced within the limits of the experimental error of the method. The technique for determining the $C_{p,m}$ according to the data of DSC measurements is described in detail in a Netzsch Software Proteus and in refs 18 and 19. The relative standard uncertainty for heat capacities was $u_r(C_{p,m})$ = 0.02. Measurements were carried out in argon atmosphere. Liquid nitrogen was used as a cryogen.

The thermogravimetric analysis of $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ over the range of (300 to 673) K was done using a TG 209 F1 Iris thermal microbalance (Netzsch Gerätebau, Germany). The thermal microbalance allows fixing the mass change within standard uncertainty $u(m) = 10^{-5}$ g. The measurement was performed with a heating rate of 10 K·min^{-1} in argon atmosphere. The measuring technique of the TG analysis was standard, according to the Netzsch Software Proteus.

RESULTS AND DISCUSSION

Heat Capacity. Experimental heat capacity data for $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ in the temperature range of (6 to 630) K are plotted in Figures 2 and 3, and given in Tables 2 and 3,

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Table 5. Smoothed Molar Heat Capacity and Thermodynamic Functions of Crystalline $Na_2Gd_2Ti_3O_{10}$ (M = 664.07 g·mol^{-1}) at Pressure p = 0.1 MPa[a]

T	$C^\circ_{p,m}$	$[H^\circ(T) - H^\circ(5)]$	$[S^\circ(T) - S^\circ(5)]$	$-\Phi^\circ_m$[b]
K	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}
5	2.06	0	0	0
10	1.39	0.00820	1.11	0.00288
15	2.82	0.0173	1.84	0.0103
20	6.652	0.05230	3.525	0.01819
25	12.57	0.08730	5.209	0.042923
30	20.22	0.1893	8.564	0.06762
40	38.27	0.4830	16.69	0.1845
50	57.92	0.9893	27.42	0.3818
60	77.94	1.619	39.36	0.7429
70	97.65	2.594	53.25	1.134
80	116.6	3.569	67.15	1.803
90	134.8	4.915	82.09	2.473
100	152.1	6.262	97.04	3.442
110	168.6	7.947	112.4	4.412
120	184.3	9.631	127.7	5.689
130	199.0	11.62	143.0	6.966
140	212.9	13.61	158.3	8.549
150	225.9	15.87	173.3	10.13
160	238.1	18.12	188.4	12.02
170	249.5	20.62	203.1	13.90
180	260.2	23.11	217.7	16.08
190	270.4	25.81	232.0	18.26
200	280.1	28.52	246.2	20.72
210	289.4	31.41	260.0	23.18
220	298.5	34.30	273.7	25.92
230	307.3	37.38	287.1	28.66
240	315.7	40.45	300.5	31.66
250	323.7	43.69	313.4	34.67
260	331.5	46.92	326.4	37.93
270	339.5	50.31	338.9	41.20
280	346.4	53.71	351.5	44.71
290	352.7	57.24	363.7	48.23
298.15	358.3	60.11	373.6	51.27
300	359.5	60.76	375.8	51.99
310	367.0	64.43	387.7	55.75
320	374.4	68.10	399.5	59.74
330	380.7	71.91	411.1	63.74
340	385.5	75.71	422.6	67.96
350	391.3	79.63	433.8	72.19
360	397	83.5	445	76.6
370	402	87.5	456	81.1
380	406	91.6	467	85.8
390	408	95.6	477	90.5
400	410	99.7	488	95.3
410	412	104	498	100
420	413	108	508	105
430	414	112	517	110
440	416	116	527	116
450	417	120	536	121
460	418	125	545	126
470	419	129	554	132
480	420	133	563	137
490	422	137	572	143
500	421	141	581	149
510	423	146	589	155
520	423	150	597	161
530	423	154	605	167
540	424	158	613	173
550	425	163	621	179

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Table 5. continued

T	$C^{\circ}_{p,m}$	$[H^{\circ}(T) - H^{\circ}(5)]$	$[S^{\circ}(T) - S^{\circ}(5)]$	$-\Phi^{\circ}_{m}$ [b]
K	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
560	426	167	629	185
570	427	171	636	191
580	428	175	643	198
590	429	180	651	204
600	431	184	658	211
610	432	188	665	218
620	434	193	672	224
630	435	197	679	231

[a]Standard for temperature $u(T) = 0.01$ K in the temperature range from $T = (5$ to $344)$ K, and $u(T) = 0.5$ K in the interval between $T = (320$ and $630)$ K. The standard uncertainty for pressure $u(p) = 10$ kPa. Combined expanded uncertainties for the heat capacity $U_c(C_{p,m}{}^{\circ})$ are 0.02, 0.005, 0.002, and 0.02; the combined expanded uncertainties $U_c[H^{\circ}(T) - H^{\circ}(5)]$ are 0.022, 0.007, 0.005, and 0.022; $U_c[S^{\circ}(T) - S^{\circ}(5)]$ are 0.023, 0.008, 0.006, and 0.023; $U_c[\Phi^{\circ}_m]$ are 0.03, 0.01, 0.009, and 0.03 in the ranges $6 \le T/K \le 15$, $15 \le T/K \le 40$, $40 \le T/K \le 344$, and $320 \le T/K \le 630$, respectively, for 0.95 level of confidence ($k \approx 2$). [b]$\Phi^{\circ}_m = [H^{\circ}(T) - H^{\circ}(5)] - T[S^{\circ}(T) - S^{\circ}(5)]$.

respectively. Heat capacities of the samples rise gradually with temperature increase over the main temperature interval. At the same time, heat capacities of both compounds were found to increase with a temperature decrease in the range of (6 to 8) K for $NaGdTiO_4$ and (6 to 10) K for $Na_2Gd_2Ti_3O_{10}$ (insets in Figures 2 and 3).

The experimental points of $C_{p,m}$ were fitted using least-squares method in the temperature range of (20 to 630) K, and the polynomial equation of the temperature dependency of $C_{p,m}$ was the following:

$$C_{p,m} = \sum_{n=0}^{k} a_i \left(\frac{T}{30}\right)^n \quad (3)$$

,where a_i are polynomial coefficients and k is the polynomial degree. The relative standard uncertainty for the heat capacities was $u_r(C_{p,m}) = 0.005$ in the temperature range of (20 to 90) K, $u_r(C_{p,m}) = 0.0025$ between $T = (80$ to $350)$ K, and $u_r(C_{p,m}) = 0.006$ between $T = (350$ to $630)$ K.

The low-temperature heat capacities of both complex oxides are found not to obey the Debye's theory. Such anomalies observed in the heat capacity curves are likely to be descending branches for magnetic disorder−order phase transitions,[9,20] which lie outside the measuring range of the calorimeter. To give the quantitative description for phase transitions under consideration, magnetic susceptibility measurements as well as heat capacity determined in an external magnetic field are required. However, according to the earlier heat capacity measurements for $NaGdTiO_4$ in the range of (0.5 to 40) K,[21] this compound shows a peak at $T = 1.74$ K originated from magnetic transition.

The identical character of temperature dependencies of heat capacities of the two titanates over all studied ranges also points out the similarity of structure of both compounds. Thus, the heat capacity of two titanates reaches the saturation level at the same temperature $T \approx 400$ K. The heat capacity of $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ coincides within an experimental error of $C_{p,m}$ measurements at $T < 12$ K, since a magnetic component[22] provides the main contribution to the total heat capacity in this range.

Standard Thermodynamic Functions. As stated above, the extrapolation of heat capacity down to $T = 0$ K was not performed. For this reason we cannot assume the residual entropy to be zero. Hence, we started to determine standard thermodynamic functions from 5 K. The calculations of $H^{\circ}(T) - H^{\circ}(5)$ and $S^{\circ}(T) - S^{\circ}(5)$ were made by numerical integration of the curves of heat capacities with respect to T and ln T, respectively (Tables 4 and 5), and Φ°_m was equal to $[H^{\circ}(T) - H^{\circ}(5)] - T[S^{\circ}(T) - S^{\circ}(5)]$. The calculation procedure was described in detail elsewhere.[23]

CONCLUSIONS

This work reports heat capacities of crystalline layered perovskite-like oxides $NaGdTiO_4$ and $Na_2Gd_2Ti_3O_{10}$ studied over the range of (6 to 630) K. Heat capacity measurements were performed by two different calorimetric methods: precise adiabatic vacuum calorimetry and differential scanning calorimetry. Heat capacity anomalies, which are likely to be associated with magnetic ordering, were observed below 8 K for $NaGdTiO_4$ and below 10 K for $Na_2Gd_2Ti_3O_{10}$. The standard thermodynamic functions of both compounds over the range of (5 to 630) K were calculated.

AUTHOR INFORMATION

Corresponding Author

*Fax: +7 831 462 35 59. E-mail: markin@calorimetry-center.ru.

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Notes

The authors declare no competing financial interest.

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